

**XRF Study in Vicinity of USS Lead
East Chicago, Indiana**

Final – November 2003

1. INTRODUCTION

This report was prepared by the U.S. Environmental Protection Agency (USEPA) to document results from the USS Lead Refinery, Inc., and Vicinity Quality Assurance Project Plan (QAPP) and associated Sampling and Analysis Plan (SAP) prepared by USEPA, dated July 2003 (USEPA 2003). The report summarizes the X-ray fluorescence (XRF) field data which were identified in the SAP as needed to further characterize the soils in the vicinity of the USS Lead Refinery, Inc. (USS Lead), in East Chicago, Indiana. The report also identifies further work to be conducted by the laboratories selected following the methods described in the SAP.

1.1 PROJECT HISTORY AND SUMMARY

1.1.1 Site History

USS Lead is a former lead smelter located at 5300 Kennedy Avenue, East Chicago, Indiana. See Figure 1. The facility was constructed in the early 1900s by the Delamar Copper Refinery Company to produce copper. In 1920, the property was purchased by U.S. Smelting, Refining, and Mining, and later by USS Lead. At that time, lead refining operations were conducted at the facility. Between 1972 and 1973, the facility was converted to a secondary lead smelter, which recovered lead from automotive batteries. In or before November 1980, USS Lead conducted hazardous waste management activities, including management of waste piles of lead dust and lead-containing calcium sulfate. Secondary lead smelting operations ceased by 1985. The constituents of concern at the site include lead, copper, arsenic, zinc, antimony, barium, cadmium, silver and tin, among others.

On November 18, 1993, USEPA and USS Lead entered into an Administrative Order on Consent (AOC) pursuant to Section 3008(h) of the Resource Conservation and Recovery Act (RCRA). The AOC requires USS Lead to implement interim measures (IM), including site stabilization and construction of a corrective action management unit (CAMU), and conduct a modified RCRA Facility Investigation (MRFI). As part of the MRFI, USS Lead conducted an off-site characterization to determine the nature and extent of contamination from its facility. The results of the investigation (see Figure 2) have indicated that airborne metal releases, mainly lead, have migrated into soils from off-site areas adjacent to the facility via the airborne pathway. However, other soil data available for a broader area in the vicinity of the facility (see Figure 3) show that lead concentrations at certain areas, including locations near residential properties, exceed 400 milligrams per kilogram (mg/kg) of lead in soil. The USEPA's Office of Solid Waste and Emergency Response recommends using 400 mg/kg soil lead as a screening level for lead in soil from residential scenarios. Screening levels are defined as a level of contamination above which there may be enough concern to warrant further investigation.

1.1.2 Sampling Area

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The SAP was implemented during the period from July 23, 2003 through August 12, 2003. The area sampled under this study is shown in Figure 1 and sample locations are further described in Table 1. The area sampled covered the Calumet and East Calumet neighborhoods of the City of East Chicago, Indiana, as well as selected industrial properties further south in East Chicago and Hammond, IN. In all, 83 soil samples were collected and analyzed, plus environmental duplicates and QA/QC samples.

1.2. PURPOSE OF STUDY

The purpose of the study was to collect information to fill data gaps identified in the SAP with respect to concentrations of metals in soil from residential and industrial properties, as well as public properties (vacant lots, parks, former industrial properties). The field data collected will be used in conjunction with laboratory data to determine if USS Lead needs to conduct additional off-site sampling to further characterize the nature and extent of off-site contamination caused by its past industrial operations. The data can also be used, in conjunction with existing data, to determine the need for remediation of soils.

To achieve the purpose, the SAP called for USEPA staff to measure concentrations of lead related to airborne deposition present in surface soil in the vicinity of the USS Lead site using the field portable Niton XRF unit (concentrations for other metals of concern including zinc were also recorded by the instrument). Upon screening with the XRF, concentrations of lead were compared to appropriate screening levels (400 ppm) to identify contamination that may pose concern. Based on the judgement of the field staff, some locations with levels of lead above the screening level were selected for sample collection to be later considered for laboratory analysis.

Information was also obtained for every screening and sampling location for development of a Geographic Information Systems (GIS) database for this project.

Laboratory analysis for lead and other metals of concern will be conducted for the samples selected, for confirmation of the XRF data. Separate analyses will also be conducted aimed at determining whether there is presence of contamination related to the USS Lead facility that warrants further investigation or whether the contaminants are related to other facilities or other anthropogenic sources. The results and interpretation of the laboratory data will be reported separately from this report.

1.3 REPORT ORGANIZATION

This report presents the field data. Section 2 discusses the methods employed, Section 3 summarizes the results, and Section 4 identifies references used. Detailed documentation is included in the Appendices.

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2. METHODS

2.1 ACCESS

Access to public and private properties in East Chicago, Indiana was acquired by USEPA personnel prior to and concurrent with implementation of the work. Access agreements in the form of consent forms were maintained on site during conduct of the work. Access was required from the following parties: private home owners and businesses, Resco Products, Inc. (former Harbison-Walker property), the City of East Chicago, the Chicago Public Housing Authority, and the EJ&E Railroad.

Since sampling was not intrusive (sampling interval limited to top 1 inch), utilities were not contacted prior to sampling.

Access agreements for all samples collected are contained in Appendix A of the report in USEPA's confidential project files, and are reserved in the final report available to the public.

2.2 SAMPLING OVERVIEW

This Section describes the soil sampling conducted during the periods of July 23-24, 2003, July 29-31, 2003, August 5-7, 2003, and August 10, 12, and 21, 2003.

Historical sampling locations from prior sampling efforts by USS Lead are shown in the SAP and on Figures 2a & 2b. Past sampling efforts by both USEPA and the Indiana Department of Environmental Management (IDEM) are shown in Figure 3. This information was used in planning this sampling event and was referred to as necessary throughout the conduct of the work.

2.3 SAMPLING PROCEDURES

2.3.1 Soil Sampling Procedures

Soil sampling was completed at 83 locations, as shown in Figures 4 through 8. All samples were collected by either Michael Mikulka or Mirtha Capiro of USEPA, or Mike Sickels of IDEM using the procedures identified in the SAP. Sample locations had not been identified in the QAPP or SAP since sample collection was dependent upon individual property owners granting access. Access was sought prior to or concurrent with each day's sampling activities, and property owners granting access usually had their properties sampled the same day or the following day, with some exceptions.

The period just prior to initiation of sampling was unseasonably wet, requiring that sampling be postponed for several days initially in order to allow the ground surface to dry. Weather

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conditions were perhaps wetter and cloudier than expected for the season throughout the sampling event. Morning temperatures each day were usually around 70-75 degrees Fahrenheit, typically warming as the day progressed. Each day was sufficiently sunny to allow air drying of samples collected prior to XRF analysis. No sampling was conducted on any day when it rained, due to uncertainties associated with sample drying in the field during rainy conditions.

Soil for screening and sample collection was composited from a residential house yard or public area (vacant lot, park, ball diamond) using a 5 point composite (see Figure 10) in accordance with procedures described in EPA Guidance Document *Superfund Lead-Contaminated Residential Sites Handbook*, OSWER 9285.7-50 (Draft) October 2002; or, for industrial property, from a one (1) square meter area (m²) area. Typically, soil was scraped from upper 1-2 inches of the target areas using a pre-cleaned disposable plastic scoop or spoon, then placed in a pre-cleaned disposable plastic bowl or other container for homogenization. If the target area was covered with grass, the grass was cut away with a knife with a stainless steel blade and pulled back to expose the soil for sample collection. At industrial properties, a stainless steel shovel was used as necessary to clear tall grass from the areas where the composite sample was collected. Approximately 4 scoops of soil were obtained from each point in the 5-point composite, for a total of 20 scoops of soil. Upon collection of the soil sample, the grass was replaced and tamped down. The bowl of sample material was transported back to the processing area, where grass, roots and rocks were removed manually (or in some cases with a Number 8 mesh stainless steel sieve), and the bowl labeled and covered with foil. If the soil was wet, the foil was pulled back and the bowl placed in the sun to allow the soil to air dry, while mixing periodically to allow drier surface soil to mix with wetter soil. Once the soil was sufficiently dry (depending on conditions, up to 4 hours drying time on some samples), 4-5 scoops of the sample were placed in a re-sealable 1 quart plastic bag for XRF analysis. All XRF screening was conducted on a bagged sample, with XRF instrument readings expressed in ppm. After screening, it was determined by the FPM in conjunction with the PM whether to proceed with sample collection for laboratory analysis based on the screening result. Initially, the plan was to collect samples for laboratory analysis from all locations where the Pb XRF screening result exceeded 400 ppm. However, based on the first few samples screened (all exceeding 400 ppm Pb) it was determined that the number of samples sent to the laboratory would far exceed the initial target and therefore the allotted budget. Therefore, sample collection was cut back to meet the minimum requirements of the study based on the SAP (confirmation for at least 10% of samples screened, and at least 1 per field day) and also provide sufficient information to ascertain possible Pb sources based on proximity to both USS Lead and other potential industrial sources. Sample collection also included field duplicate collections from locations S03 & S07 (samples D03 & D07), and matrix spike/matrix spike duplicate (MS/MSD) sample collection from location S07 (sample M07).

Photos of each of the samples were not taken, in order to speed up the sampling process, and because photographs of each sample location did not appear to materially add to the information being collected. A log of the photographs as well as all the photographs taken, are shown in Appendix B.

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Upon completion of sample processing, if soil screening levels for lead exceeded 400 ppm, and the sample location also met other goals of the project, then sample bottles were prepared from the sample bowl. Section 3.2 of the SAP, Selection of Screening and Sampling locations, explains the rationale for proceeding with sample collection for consideration for laboratory analysis. Upon filling and labeling, the sample bottles were placed in an iced cooler within the vehicle used for equipment storage and remained within the custody of the processing personnel. Splits of samples collected were offered to personnel from Resco, but they declined.

On August 7, 2003, those samples for which processing was not able to be completed before the end of the day were covered with foil, labeled, and placed in coolers filled with ice for secure storage at the USEPA CRL. On August 10, 2003, air-drying and processing of the samples was continued, and the samples were analyzed by Mirtha Capiro of USEPA with the Niton XRF instrument.

Re-sampling was conducted at certain XRF screening locations that were not originally selected by the FPM for sample collection for laboratory analysis, but were later determined by the PM (after review of all XRF data) to be appropriate locations for sample collection, mainly to attempt to confirm the source of the Pb. Locations X07 and X08 were re-sampled on August 12, 2003, and location X20 was resampled on August 21, 2003, by Mirtha Capiro of USEPA. Re-sampling included 5 point composite sampling and homogenization as per the SAP, but did not include XRF screening. As such, the laboratory results from these samples will not be directly comparable to the XRF results, as they are not from the same sample. These 3 samples should be considered co-located samples to the samples which were screened by the XRF.

2.3.2 Horizontal Location Control

USEPA personnel identified the location of each soil sample collected for XRF analysis with a flag labeled with the XRF location number, as per the SAP. Locations were concurrently or later recorded by USEPA personnel using a Trimble global positioning system (GPS) unit. GPS coordinates were recorded within the instrument and later downloaded into a spreadsheet. Table 1 identifies the specific locations of each soil sample collected for XRF analysis.

2.3.3 Sample Logging

The specific property address where each composite sample collected for XRF analysis was taken was also noted in the field log book. Each location was identified with a unique identifier (XRF #) and its general location described in the field log book. Sample locations relative to the house and other structures are shown in the field log book and sometimes also on the consent form/access agreement. Copies of the consent forms are contained in Appendix A (reserved). Information on the properties sampled is contained in Table 2 and Appendix E (reserved). A copy of the field notes are contained within the USEPA project files.

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2.3.4 Deviations from the SAP

During the first day of project field activities, it was decided by the PM in conjunction with the FPM that individual samples would not be photographed, and the locations where the samples were collected would also not be photographed. An address of each location is provided in the field logbook and on the consent form should further access or information about any specific property be necessary. A log of all photographs taken as well as the photographs, are contained in Appendix B. The photographs show the typical sample and screening using the XRF unit. This was considered sufficient for project purposes.

Initially, the plan was to collect samples for laboratory analysis from all locations where the Pb XRF screening result exceeded 400 ppm. However, based on the first few samples screened (all exceeding 400 ppm Pb) it was determined that the number of samples sent to the laboratory would far exceed the initial target and therefore the allotted budget. Therefore, sample collection was cut back to meet the minimum requirements of the study based on the SAP (confirmation for at least 10% of samples screened, and at least 1 per field day) and also provide sufficient information to ascertain possible Pb sources based on proximity to both USS Lead and other potential industrial sources. Section 3.2 of the SAP, Selection of Screening and Sampling locations, explains the rationale for proceeding with sample collection for consideration for laboratory analysis.

Re-sampling was conducted at certain XRF screening locations that were not originally selected by the FPM for sample collection for laboratory analysis, but were later determined by the PM (after review of all XRF data) to be appropriate locations for sample collection, mainly to attempt to confirm the source of the Pb. Locations X07 and X08 were re-sampled on August 12, 2003, and location X20 was resampled on August 21, 2003, by Mirtha Capiro of USEPA. Re-sampling included 5 point composite sampling and homogenization as per the SAP, but did not include XRF screening. As such, the laboratory results from these samples will not be directly comparable to the XRF results, as they are not from the same sample. These 3 samples should be considered co-located samples to the samples which were screened by the XRF.

No other deviations from the approved SAP were noted.

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2.4 LABORATORY ANALYSES

Samples were collected to be considered for laboratory analyses from 29 locations out of the 83 locations screened using the XRF (about 35%). Of those locations, considering the results of the XRF data and the overall project objectives, 20 locations (about 24%) were selected for laboratory analyses of fine and residual fractions for semi-quantitative scans for target metals and lead isotopes, and quantitative scans for selected metals by American Analytical & Technical Services (AATS). In addition, the same 20 locations were selected for electron microprobe analysis (EMPA) by the Laboratory for Environmental & Geologic Studies (LEGS). The EMPA will provide information on the morphology and chemical composition of individual particles within a sample. See Table 4a for a listing of these locations. One duplicate sample (D03) was selected from location S03 to be analyzed by AATS and by LEGS, to meet project QA/QC objectives for duplicates. A sample (M07) was collected for MS/MSD analyses by AATS to meet project objectives for MS/MSD. If matrix spike samples are required by the method used by LEGS, the laboratory has been directed to use available sample volumes to generate its own MS/MSD sample. In addition, a rinsate blank sample (R01) was collected to be analyzed for target metals by EPA Method 6020 by AATS. Samples which will not be analyzed at this time are being stored at USEPA's Central Regional Laboratory in its secure sample storage area. A list of those samples is contained in Table 4b.

A chain-of-custody record for each set of samples was maintained throughout all sampling activities and accompanied samples to the laboratory. See Appendix C.

2.4.1 Laboratory Protocols

The specific analytes requested for each sample are identified in Table 5. Table 5 in the SAP identifies the analytical methodology and target detection limits for each parameter.

2.4.2 Deviations from the SAP

The SAP identified that samples would also be collected and analyzed by X-Ray diffraction (XRD) by EPA's National Risk Management Research Laboratory (NRMRL), to identify lead species. After the first two days of sampling, discussions with the NRMRL revealed that such analyses would not yield useful results if the lead values were less than 10,000 ppm. In light of the results (all samples <2,000 ppm), further efforts to collect samples for XRD analyses by NRMRL were abandoned. This deviation was documented in a telephone conversation record in the field log book, and in Addendum 01 to the QAPP dated September 2003.

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3.0 RESULTS

3.1 XRF RESULTS

XRF readings were taken for 83 locations. Lead results for each location are shown in Table 3.

Based on the theory of operation of the XRF instrument, data for which the value recorded is less than 3 times the standard deviation (σ) of the XRF readings are considered invalid. For example, if the average of the Pb XRF readings after 60 seconds of instrument operation is 100 ppm, and the standard deviation of all the readings resulting in the 100 ppm reading is 60 ppm, then that reading is not considered valid. Similarly, those with a recorded XRF value between 3σ and 10σ are considered quantitatively uncertain, and those with values greater than 10σ are considered valid readings. Generally, longer readings using the instrument yield a lower σ , and hence more useful data. For the purposes of this study, a 60 second reading time (or greater) with the XRF generally yielded usable results for lead (Pb). Where Pb readings were low (< 100 ppm), a longer time was usually necessary in order to generate a reading greater than 10σ . If after a longer reading time this still did not occur, the Pb values presented in Table 3 and elsewhere in this report are considered quantitatively uncertain, since $3\sigma < \text{result} < 10\sigma$. In no case was the Pb result for any sample $< 3\sigma$, so the data collected using the XRF instrument for Pb in this study are of excellent quality. Pb results from the XRF are shown in Figures 4a and 4b for all sample locations.

The XRF instrument was able to collect data for the following other metals in addition to Pb: Iron (Fe); Zinc (Zn); Zirconium (Zr); Rubidium (Rb); Molybdenum (Mo); Strontium (Sr); Selenium (Se); Arsenic (As); Mercury (Hg); Copper (Cu); Nickel (Ni); Cobalt (Co); Manganese (Mn); and Chromium (Cr). For most samples, valid data were generated by the XRF for only Pb, Fe, Zn, and Zr. Typically, other metals did not meet the $>10\sigma$ criterion necessary for valid results. The results for Rb were typically quantitatively uncertain. See Appendix E for all results on all metals.

Figures 5a and 5b show the results for Zn. Figures 6a and 6b show the results for Fe. Figures 7a and 7b show the results for Zr. Figures 8a and 8b show the results for both Pb and Zn as it was thought useful to see the results for these two metals together.

Actual XRF reading results for each day of sampling are contained in Appendix E. Tables E-1 through E-3 report all XRF readings recorded during the study. An electronic version of the data is also contained in Appendix F.

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3.2 XRF DATA QUALITY

Quality control checks were run throughout the course of the study to ensure the data being collected by the XRF unit were of sufficient quality. Each day, the instrument was turned on and self-calibration conducted. Upon completion, the unit would indicate it was ready for bulk sample analysis.

At that point, a bag blank was run to verify the instrument was reading properly at the low end. The bag blank was an empty sample bag placed on a wooden cutting board and run for at least 30 seconds. The only metal thought to be in the empty bag at low concentration was zinc, and this proved to be correct. Bag blanks were found acceptable if all readings recorded were at $< \text{LOD}$ (level of detection) or $< 3\sigma$. If this did not occur, the instrument and cutting board were cleaned using a paper towel sprayed in distilled, de-ionized water generated by EPA's Central Regional Laboratory (CRL). The bag blank was then re-run and considered acceptable if all readings recorded were at $< \text{LOD}$ or $< 3\sigma$. Results of all bag blank samples are contained in Appendices E & F.

The next quality control check run was an XRF analysis of a Standard Reference Material (SRM) of known concentration, which was then compared to the certified values for the reference material. In this case the SRM used was SRM 2711, a Montana soil. The certified results for the SRM 2711 are contained in the SAP and in Appendix D to this report. The sample of the SRM was contained in a plastic cup specifically designed for use on the Niton soil testing platform. The SRM was acquired for use and prepared for the field effort by John Morris of USEPA's CRL. SRMs were run at the beginning and end of each day to ensure the instrument was working properly. The SRM check was considered acceptable if the XRF result for Pb plus the standard deviation of the result was within the low range of the certified standard. Otherwise, the XRF results should be expected to have a low bias. Results of all SRM quality control checks are shown in Appendices E & F.

If the self-calibration, bag blank, and SRM were all acceptable, then samples were ready to be analyzed by the XRF instrument. This occurred on all days of testing. The only difficulty encountered with the daily quality control checks was with the SRM testing on day one. It was realized after several attempts with unacceptable results that the SRM had to be run using the soil testing platform, but without the shield used for testing normal bulk samples, as the testing platform contains its own shield. This explains the invalid SRM testing results obtained at the beginning of day 1 of testing.

The final field quality control check was a daily precision test run on one individual sample selected due to its Pb level exceeding the 400 ppm screening level. The purpose of the precision sample was to verify proper homogenization of field samples, and that the XRF reading was a true representation of the Pb concentration in the bagged samples. Each precision test was run using at least 7 XRF readings on the selected sample. Validity of the results were evaluated by

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calculating the relative standard deviation (RSD) of the 7 sample results as per the procedure specified in the QAPP. The results of the precision samples for the 9 days of XRF analysis are shown in Table 6. All results were within the acceptance range for the RSD specified in the QAPP except the results for Pb on July 30, 2003. The RSD for that date was 26.5% vs. the <20% acceptance criterion. The quality of XRF results for that date are still considered acceptable, however, as the poor result for the precision sample was due due to one high reading (R50, XRF result for Pb of 856 ppm) in the precision set. All other readings for the location X36 for which the precision sample was run were in the range 452-610 ppm. If that one outlier is excluded, the precision criterion for the sample was met.

Bag blanks were run periodically throughout the course of each sampling day, to verify the instrument was still functioning properly. If the result on the bag blank showed elevated levels of any metals, the instrument, shield and cutting board used as a sampling platform were all cleaned using distilled, de-ionized water. Then the bag blank test was rerun using a new clean bag.

The final quality control check will be the laboratory confirmation samples sent to AATS for analysis. All samples were transferred via chain-of-custody to TechLaw for shipment to the laboratory on August 28, 2003. See Appendix C.

3.3 PROJECT DATA BASE

A project database, containing an electronic version of the data and other relevant project information, is contained on a CD as Appendix F.

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4.0 REFERENCES

USEPA Technology Innovation Office, web site on X-Ray Fluorescence, http://fate.clu-in.org/xrf_main.asp

USEPA 2003a. Quality Assurance Project Plan USS Lead Refinery, Inc. & Vicinity, East Chicago, IN. July 2003.

USEPA 2003b. Field Sampling and Analysis Plan USS Lead Refinery, Inc. & Vicinity, East Chicago, IN. July 2003.

USEPA 2003c. Addendum 01 to Quality Assurance Project Plan USS Lead Refinery, Inc. & Vicinity, East Chicago, IN. September 2003.

USEPA 2002. *Superfund Lead-Contaminated Residential Sites Handbook*, OSWER 9285.7-50 (Draft) October, 2002.